

**Department of Energy**

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10 JUL 2003



Mr. Steve Zappe, WIPP Project Leader  
Hazardous Waste Bureau  
New Mexico Environment Department  
2905 Rodeo Park Drive East, Bldg. 1  
Santa Fe, New Mexico 87505-6303

Subject: Response to NMED Observer Inquiries

Dear Mr. Zappe:



The Carlsbad Field Office (CBFO) appreciates the New Mexico Environment Department's (NMED's) clarification of two inquiries expressed during the audit performed by CBFO at the Rocky Flats Environmental Technology Site (RFETS) on March 6, 2003. After evaluating NMED's response (letter dated April 28, 2003) to the CBFO's explanation of these issues, in addition to engaging in subsequent e-mails and conversations with Mr. Bob Thielke, it continues to be CBFO's contention that the tentatively identified compound (TIC) and Contract Laboratory Program National Functional Guidelines (CLP) issues are both addressed in a manner that is compliant with the permit.

With regard to the TICs inquiry, it is CBFO's position that the investigation of the source of the TICs was appropriately evaluated. The acceptable knowledge record was reviewed and those chemicals were not found to be identified as part of the waste stream. A subsequent review of the literature concerning thermal destruction process has indicated that it is not unexpected that volatile organic compounds (VOCs) might be generated during operations (See Enclosure 1). It is therefore appropriate to attribute the TICs to "other origins" as allowed in Section B3-1 and therefore not add them to the target analyte list. We have also considered Mr. Thielke's response to our white paper (See Enclosure 2) and it is CBFO's position that no further analysis is necessary. As stated above, the process implemented at RFETS is compliant with the provisions of the permit.

With regard to the CLP issue it is CBFO's position that there are no requirements in the permit mandating the issuance of data usability criteria beyond those already specified in the permit (Attachment B3). Therefore, for those limited instances where data usability issues, beyond those specifically addressed in the permit, must be handled CBFO will mandate the implementation of the CLP Functional Data Validation Guidelines for Inorganic and Organic Analysis. Nothing in the CLP guidelines will supercede the *Hazardous Waste Facility Permit* "Waste Analysis Plan" (WAP) requirements.



Mr. Steve Zappe

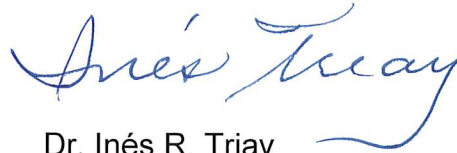
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As explained in CBFO's responses to NMED's observer inquiry on this issue, the use of these guidelines is acceptable and appropriate. In addition, these guidelines are consistent with the Corp of Engineers data usability guidelines that Mr. Thielke recommended CBFO read. In fact, these references address the subjective nature of assessing data usability and recognize the need for professional judgment.

Once again, thank you for your input regarding these issues. If you need any further information, please contact Mr. Kerry Watson at (505) 234-7357.

Sincerely,



Dr. Inés R. Triay  
Manager

Enclosures

cc: w/o enclosures  
K. Watson, CBFO  
S. Martin, NMED  
M. Doherty, Tech Specs  
K. Lickliter, Tech Specs  
CBFO M&RC

**Enclosure 1**

June 3, 2003

## **VOC TICs in SVOC ANALYSES**

Volatile Organic Compounds (VOCs) have appeared as tentatively identified compounds (TICs) during analysis of samples using SW-846 Method 8270C. The analytical method and the preparation steps for this method are used to quantify semi-volatile organic compounds (SVOCs), and as such, it is not expected that VOCs would survive the sample preparation techniques. This paper will explain why VOCs may be identified in the waste matrix using Method 8270C, and why adding the VOCs to the target analyte list for SVOCs is not advisable.

## **PRODUCTS OF INCOMPLETE COMBUSTION**

Thermally treated waste streams that are under consideration for the WIPP site are wastes that have been treated to reduce volume or to facilitate plutonium recovery. These processes were not operated solely to destroy hazardous organic compounds. It is therefore not expected that these processes would completely eliminate organics. Thermal processes and chlorine-containing waste are known to produce new species of hazardous organic compounds in the effluent (EPA). These compounds are called "products of incomplete combustion" (PICs), even if the process is not incineration.

When waste is subject to thermal processes, such as incineration or kilning, hazardous compounds in the waste may not breakdown completely or they may recombine and form totally new species (Rogers and Willis, EPA). The process of recombination is not reliably predictable. It is expected that processes that are underventilated or otherwise configured for less than optimal thermal destruction will have numerous organic species in the output (flue gas, particulates entrained in the flue gas, and ash). It has been demonstrated that these compounds will be found adsorbed to the ash and particulate matter (Tolocka and Miller).

The EPA has attempted to identify a list of PICs important to hazardous waste combustors (EPA). The cited paper performed both VOC and SVOC analyses. The samples were taken from the effluent gases. These gases included entrained particulates. While this is not the same as the process ash, it will serve in this paper to show that VOCs can be found in the SVOC results as TICs.

The paper identifies several of the subject compounds as VOC target analytes (trichloroethylene, trichloroethene, 1,1,2-trichloroethane, and 1,1,2-tetrachloroethane). These compounds were generally not detected in the VOC analyses. The SVOC preparation method included Soxhlet extraction. The subject compounds were not listed as SVOC target analytes. 1,1,2-trichloroethane was found as a TIC once in 15 runs. Tetrachloroethane was found twice. (EPA)

These references demonstrate that thermal processes that include chlorine will produce chlorine-containing compounds as PICs. The processes involved in breaking bonds and reforming other bonds is complex and can result in a number of possible products, including those found as TICs in waste samples. It is also understood that these PICs can adsorb to particulate matter as well as become physically entrained in the matrix. While the sorbed species lend themselves to quantitation by a variety of methods, the entrained species do not. Two of the species observed have no support from AK or packaging and seem likely to have arisen during the thermal processing, 1,1,1,2-tetrachloroethane and 1,2,3-trichloropropane. All of the species may have arisen from the thermal processing because the feed material contained appreciable quantities of polyvinyl chloride (from glovebox bag-out bags).

## ANALYTICAL METHODS

VOCs that appear as TICs in the SVOC analytical methods are compounds that have been liberated from entrainment in the waste matrix and have survived the sample preparation process. This is confirmed by the lack of detection of these compounds in the blank samples. There are two questions to answer; is there a sample preparation method suitable for these waste matrices that can be used with the VOC analytical method and, is there a suitable SVOC preparation method that will provide adequate results for adsorbed VOCs?

### SW-846 Sample Preparation for Method 8260B (VOCs)

The sample preparation methods for Method 8260B are outlined in Method 5000. There are six methods suitable for solid matrices. There are others that are used to desorb samples from sampling material such as sampling train cartridges and for gas samples. These methods generally rely on the volatility of the compounds to extract them from the waste matrix. Several of the methods require the compound to purge from the waste at temperatures below 85 degrees centigrade. One method is used to dilute the waste sample in hexadecane and directly inject it into the instrument.

The TICs at issue are chlorinated compounds that were generated during the thermal treatment process and then entrained in the waste matrix. If they were simply adsorbed on the surface, they would have been detected in the headspace gas sampling. This leads to the conclusion that the chlorinated hydrocarbons are physically entrained (within microscopic closed-cells present in fly-ash). The species of interest are not extractable without completely dissolving the matrix, or crushing it to the extent that the closed-cells are ruptured. (This entrainment phenomenon is why the ash recovery process at Rocky Flats was so difficult to achieve, and is the reason the backlog of ash accumulated at Rocky Flats.) The energy required for this extremely vigorous process of matrix dissolution/destruction would greatly exceed that required to drive the liberated chlorinated organics from the matrix. The preparation methods cited for Method

8260B are not sufficiently robust to quantitatively free the compounds from the waste matrix. The preparation methods rely on the inherent volatility of the compounds and are rigorous enough to overcome the attraction of the PIC to the waste matrix. This is supported by the lack of detection of the VOCs in the waste samples.

#### SW-846 Sample Preparation Methods for Method 8270C (SVOCs)

It is not known but likely that the subject VOC TICs could be acceptably calibrated for analysis using Method 8270C. The surrogates and matrix spikes may not be a reliable indicator of the expected analyte recovery since these standards are not mixed with the waste matrix under the same extreme conditions as the thermal process that generated the waste. The standards are mixed with the surrogate matrix at room temperature; however they are subject to the sample preparation steps. The high temperatures involved are expected to drive off most of a VOC standard, which is why this method is not generally suitable for analysis of VOC compounds.

The sample preparation methods that are used with Method 8270C are found in the Method 3500 series. All of these methods include an initial step where the sample is cut, chopped, or ground to a fine particulate. The sample is then subjected to high temperatures and strong acids (except for supercritical fluid extraction, Method 3561). These conditions will compromise the defensibility of the VOC results even though they may be tightly bound to the waste matrix and can be detected in the analyses. Because of the sample preparation techniques, it is not possible to determine what fraction of the VOCs were lost during preparation and which fraction remains bound to the waste matrix and is discarded. Without knowledge of these fractions, the fraction measured in the sample extract cannot be accurately related to the original concentration. SW-846 does not provide a sample preparation method that would appear to preserve the VOCs while also extracting them from a strong attraction to the waste matrix.

#### WASTE CHARACTERIZATION

The appearance of VOC TICs in SVOC results but not in VOC results raises the question of whether the waste was properly characterized. All waste in Summary Category Groups S3000 and S4000 are characterized using acceptable knowledge. That characterization is confirmed with sampling and analysis. Hazardous waste constituents that are identified in the AK reports will result in the application of listed waste codes (F, U or P) regardless of the analytical results.

When TICs are identified in a waste stream, the site attempts to identify the source of the TIC. Often the TIC is a compound that has been identified as a waste component. If so, the waste will already carry the appropriate hazardous

waste codes. It is also likely that the source of the compound can be traced to waste packaging materials. If so, the waste will generally not be assigned a listed waste code. The last option is to determine if the compound can be attributed to radiolytic degradation or some other origin. Failing this, the site is obligated to assume the compound is from an F-listed waste (if it is a constituent compound in an F-listing). Sites can generally rule out U and P listings for the compound by acceptable knowledge. (The current WAP requirement to investigate the source of the TIC would identify waste that should carry these codes; therefore, the language centered on F-listed TIC does not require change.)

If a VOC TIC that is a listed hazardous waste constituent is identified with the SVOC method, it could result in a new code being applied to the waste stream. If the TIC meets the criteria in the Waste Analysis Plan, it will be evaluated to determine the possible source. Sites conservatively assign hazardous waste codes; therefore, if the compound cannot be attributed to waste packaging or other origins, the applicable hazardous waste code is applied. That VOC would be added to the VOC target analyte list also.

In the case of waste from thermal processes where VOCs are detected in SVOC analyses, it is possible to attribute their presence as due to other origins, namely as PICs. If the AK record has already established the compound as a constituent of the waste, no characterization change is required. If the compound has not been identified in the AK record but is a constituent of an F-listed waste, the code would be applied to the waste stream. If the compound is an Appendix VIII compound but does not have an associated code, the compound would be attributed to other origins, and not added to the target analyte list as allowed by WAP B3-1.

## REFERENCES

EPA. *Development of a Hazardous Waste Incinerator Target Analyte List of Products of Incomplete Combustion*. Office of Solid Waste, EPA/600/R-98/076, June 1998.

Rogers, H.W and Willis, B.C. Agency for Toxic Substances and Disease Registry (ATSDR). Public Health Overview of Incineration as a Means to Destroy Hazardous Waste. <http://www.atsdr.cdc.gov/HAC/hwincin.html>

Tolocka, M.P. and Miller, J.H. *Production of Polycyclic Aromatic Hydrocarbons from Underventilated Hydrocarbon Diffusion Flames*. Proceedings: Combustion Institute/Eastern States Section, Chemical and Physical Processes in Combustion, Fall Technical Meeting, October 16-18, 1995. Worcester, MA.

**Enclosure 2**



## MEMORANDUM

**TO:** Mark Doherty  
**FROM:** Robert Thielke  
**DATE:** June 3, 2003  
**SUBJECT:** Additional Questions Regarding Formation of VOCs as a Result of Incomplete Combustion of RFETS Solids

Thank you for your initial technical explanation regarding the presence of VOCs in the thermally processed solids from RFETS. We agree that it is possible that the VOC TICs that were found in the SVOC analysis could be products of incomplete combustion (PICs). We do require, however, additional information pertinent to major points raised in your paper.

### **1. Additional Incomplete Combustion Information**

Specific *de novo* formation of halogenated aliphatic compounds as PICs is dependent upon several waste and combustion conditions. The specific conditions that are critical to the formation of halogenated aliphatic PICs include:

- An adequate source of chlorine atoms during the incineration process
- An adequate source of carbon in the appropriate matrix during the incineration process
- The appropriate percentage of available oxygen in the incineration process
- An appropriate catalyst metal for the formation of halogenated aliphatic compounds
- An appropriate incineration temperature range in which aliphatic PICs would be created.

Demonstrating that generation of SVOC TICs through incomplete combustion (creating PICs) would require assembly and analysis of data to ensure appropriate chlorine, carbon and oxygen sources were present, as well as catalyst metal and incineration temperatures. Therefore, for each of the solids waste streams at RFETS, we would need to see information derived from the AK records or VE/RTR at RFETS which shows that appropriate conditions existed during incineration to result in the formation of these halogenated aliphatic PICs. Following is a brief overview of the type of information and evaluation that should be provided for each of the solids waste streams at RFETS. Note that we do not expect exhaustive data analysis; enough information is required, however, to demonstrate that adequate sources, catalysts, and temperatures were achieved to create these compounds.

a. *An adequate source of chlorine atoms* - Identify chlorinated compounds that were known to be in the waste, including any associated hazardous waste codes that have been assigned to the waste stream because of the chlorinated compounds. Additionally, some examination must be made to determine if adequate amounts of chlorinated compounds were present in the waste prior to incineration to provide an adequate source of chlorine to account for the moles of chlorine found in the TICs. We understand that detailed mass balances would not be feasible; instead, we are looking for a general, higher-level analysis (i.e., a rough molar balance) to support your contention that adequate chlorine was available in the waste prior to incineration. The potential for other sources of chlorine in the incineration process should also be explored, as it may help demonstrate that adequate chlorine was available during the incineration process to generate these PICs.

b. *A source of carbon* - As with the chlorine, provide a higher-level (i.e., rough molar balance) demonstrating that adequate sources of carbon were available for each of the waste streams. Sources of carbon can include but may not be limited to organic compounds present in the waste prior to incineration (hazardous and non-hazardous), the composition of the waste matrix (i.e., cellulosic compounds), and any incidental packaging materials used in the incineration process. Additionally, the form of the carbon is critical to *de novo* formation of organic compounds, as not all forms of carbon are amenable to the formation of organic compounds. The discussion should verify that the forms of available carbon are amenable to PIC formation.

c. *An oxygen source* - Oxygen is needed to trigger the kinetic reactions that occur to form compounds in the incineration process. Excess or insufficient oxygen in the incineration process can have critical impacts on the extent to which PICs can be formed. Provide additional discussion for each of the waste streams to demonstrate that an optimal oxygen percentage was available during the combustion process to cause incomplete incineration to occur. The discussion need only be qualitative in nature, including a general discussion of the incineration process to identify process steps that could result in incomplete incineration. For example, incomplete incineration in a process flow incineration process can occur if the waste feed stream velocity is too high or if the fuel feed stream is too slow. However, these qualitative assessments of the process must be consistent with the normal operation of the incinerator for its intended purpose.

d. *An appropriate catalyst metal* - Formation of PICs in the quantities found in the SVOC TICs is highly dependent upon the availability of the appropriate catalyst metals. Several metals serve as excellent catalysts for the formation of halogenated aromatic compounds. However, the available literature indicates that only specific metals are suitable for the *de novo* formation of

halogenated aliphatic compounds as a result of incomplete incineration. For each waste stream, indicate the catalyst metals that were available in the waste in sufficient quantities to facilitate the formation of halogenated aliphatic compounds. Associated metals analyses would serve as an excellent source of information to identify metals that are present in each of the waste streams. In addition, it would be helpful to cite literature that indicates the acceptability of a particular metal in the waste as catalyst for the formation of halogenated aliphatic compounds.

- e. *The optimum temperature for halogenated aliphatic formation* - If adequate carbon, chlorine, and catalyst are available, halogenated aliphatic PICs can form within specific temperature ranges. Provide adequate information to demonstrate that the incineration process operated within the optimal incineration temperature range to facilitate the formation of halogenated aliphatic compounds.

## **2. Additional Evaluation**

To ensure that the formation of TICs/PICs and the ramification of their identification are adequately addressed, the following must also be addressed:

- Although the AK records at RFETS that were provided during audits indicate that no additional materials were added to the waste before or during the incineration process, the practice of adding materials to facilitate incineration does occur. For example, Washington State Department of Ecology representatives indicated that oils were added to the incineration process at Hanford prior to incineration. Additional research into RFETS incineration with respect to the addition of such facilitating materials during incineration of other thermal treatment processes is warranted.
- Hanford is currently storing incinerator ash that originated at RFETS. However, the RFETS ash at Hanford underwent a secondary calcining process after receipt at Hanford, apparently to make the waste more brittle for future processes and to address radiolysis issues. A comparison of chemical data and analytical results between Hanford and Rocky Flats may provide additional information with respect to the formation of PICs, as well as potential contributions due to radiolysis. Issues that should be examined include but not be limited to:
  - Comparison of Hanford-RFETS analytical HSG results, particularly comparing results from RFETS wastes that were not calcined to wastes stored at Hanford that were calcined.
  - Comparison of calcined waste and un-calcined waste to determine if there are any chemical and physical differences

- Comparison of the incineration process at RFETS to the calcine thermal process at Hanford to evaluate the extent to which incomplete combustion could occur in each of the processes.
- Effect of calcining on radiolysis, and nature of constituents generated via radiolysis in the RFETS ash stored at Hanford prior to calcining taking place. Assess whether similar problems occurred at RFETS (it is our understanding that RFETS waste was vented, so gaseous build-up was not necessarily an issue).

For waste streams in which you have determined that incomplete combustion likely occurred, address the following concerns:

- The same conditions that are amenable to the formation of halogenated aliphatic PICs are also amenable to the formation of halogenated aromatic compounds. In light of this, discuss the presence or absence of aromatic and polyaromatic hydrocarbons in the sample analyses (particularly SVOCs). Any limitations of the analysis to detect heavier molecular weight polyaromatics should be provided.
- Dioxins and furans are also likely byproducts of incomplete incineration. Discuss, from a waste management and regulatory perspective, any concerns that may arise from the disposal of wastes that contain dioxins and furans. Discuss from a technical perspective if these compounds could also be formed as a result of incomplete incineration, and if so what regulatory obligations CBFO has in terms of waste characterization, management, and disposal.
- Address how incomplete combustion of materials relates to specific permit conditions requiring that thermal treatment processes must result in the reduction of matrix-related VOCs, etc. Specifically, address how available information, including the identification of TICs in solid matrices and the subsequent assignment of hazardous waste codes, comports with the reduced headspace gas sampling requirement in Section B-3a(1)(ii) that "the waste stream must have either been generated using a high-temperature thermal process, or been subjected to a high-temperature thermal process after generation that resulted in the reduction of matrix-related VOCs in the headspace". Discuss whether VOCs were detected in headspace (data indicate this may be the case, but this should be updated to include recent information). Note that this is being requested to address potential questions concerning the presence of hazardous waste within a "high temperature" waste stream, as this would bring to question whether the "high temperature" was high enough if incomplete combustion occurred.
- Address whether the formation of hazardous constituents (and subsequently hazardous waste codes) as PICs during thermal processing

is "exempt" from regulation as a hazardous waste under RCRA. This is important because you wish to argue that the formation of PICs constitutes an "other" process that would exempt the addition of the TIC constituent to target analyte lists and, hence, remove the constituent for consideration as a potential hazardous waste. This approach should be assessed with respect to how this situation is "handled" at other RCRA facilities where waste is thermally processed, but not treated to RCRA (LDR) requirements. It is our understanding that generation of new hazardous constituents in waste processed for purposes other than RCRA treatment (which the RFETS waste falls under) should be assessed as to whether the constituent generated would mandate the addition of codes as per the definition of those codes under RCRA. You have done a good job explaining the addition of codes as per the permit, but do need to go a step further in addressing this important aspect.

### **3. Other Comments**

In response to the other elements of your correspondence, we have the following comment:

We believe that the available SW-846 SVOC sample preparation methods would not drive off spike and surrogate compounds that were added to samples to accommodate additional target compounds identified through the TIC identification process. Surrogates and spiking compounds are added to the sample after the particle size reduction has occurred. Therefore, the rigorous sample milling that apparently released the entrained organic compounds would not impact the recovery of spikes and surrogates. The SVOC sample preparation methods referenced in SW-846 primarily have the potential to lose spike and surrogate constituents when the extract is heated during the extract concentration process, and at that point the potential for analyte loss of the spikes and surrogates should be equivalent to that of the analyte in the sample that these spiking analytes are intended to represent. As indicated in our meeting that occurred on May 29, 2003, there are several compounds that appear on both the SW-846 Method 8260 and Method 8270 target lists, and that these compounds that appear on both target lists have physical characteristics that are comparable to the compounds identified as TICs in the SVOC analysis. There may be instances in the future where a VOC target compound may be found as an SVOC TIC and may not be amenable to SVOC analysis. However, it is more likely that these compounds would be lost during the extract concentration step; and as a result would not appear as a TIC in the SVOC analysis. Under any circumstance, the permit does not include any specific provisions for waiving the TIC reporting criteria for adding TICs to the SVOC target list based upon the TIC being classified as a volatile compound; and RFETS is still obligated to add the TICs to the SVOC target list. Additionally, in the event any concerns over inadequate matrix spike or surrogate recoveries associated with these additional

compounds added to the SVOC target list would likely be favorably mitigated during the data usability analysis and found to be usable (citing limitations of the method in recovering SVOC matrix spike compounds associated with the VOC TICs that were added to the SVOC target list).

If you have any questions regarding this memorandum, please feel free to call me directly at 303-763-8881 or email me at [ritattea@msn.com](mailto:ritattea@msn.com) . I look forward to your response to these additional questions and having the opportunity to adequately resolve these issues.